(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 249 533 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
16.10.2002 Bulletin 2002/42

(51) Int Cl.7: D21H 23/48, D21H 19/82

(21) Application number: 01109266.5

(22) Date of filing: 14.04.2001

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE TR
Designated Extension States:
AL LT LV MK RO SI

(71) Applicant: THE DOW CHEMICAL COMPANY
Midland, Michigan 48640 (US)

(72) Inventor: Urscheler, Robert
8810 Horgen (CH)

(74) Representative:
Sternagel, Fleischer, Godemeyer & Partner
Patentanwälte
Braunsberger Feld 29
51429 Bergisch Gladbach (DE)

(54) Process for making multilayer coated paper or paperboard

(57) The present invention refers to a method of manufacturing multi-layer coated papers and paperboards, but excluding photographic papers and pressure sensitive copying papers, that are especially suitable for printing, packaging and labeling purposes, in which at least two coating liquids selected from aqueous emulsions or suspensions are formed into a composite, free-falling curtain and a continuous web of basepaper or baseboard is coated with the composite coating liquid and paper or paperboard thereby obtainable.

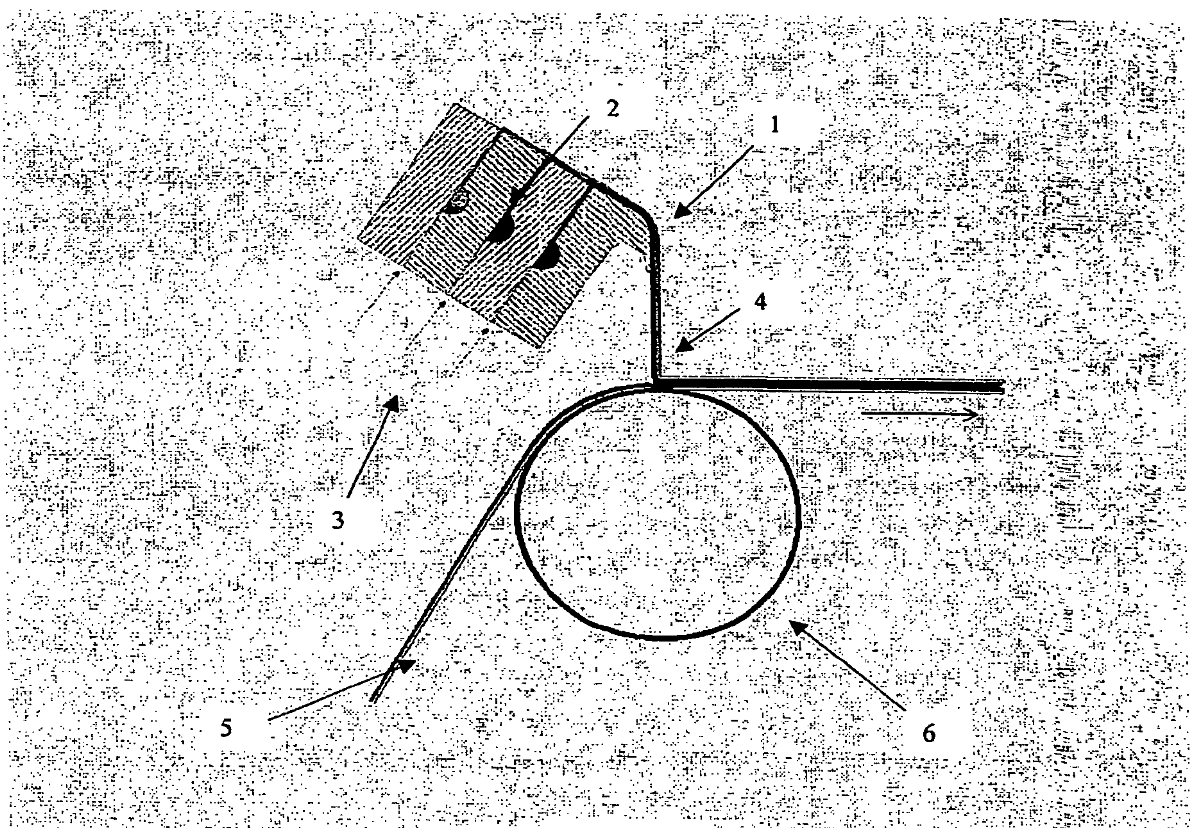

Fig. 1

EP 1 249 533 A1

Description

Field of the Invention

[0001] This invention relates to a method of manufacturing coated paper and paperboard whereby multiple layers of coating liquid are applied simultaneously to a rapidly moving, continuous web of paper or paperboard substrate by curtain coating. More specifically, the present invention relates to a method of manufacturing multi-layer pigment coated paper and paperboard such that the coated surface gives superior suitability for printing than multi-coated papers and paperboards produced using sequential applications of single layers of coating applied by single-layer curtain coating or single-layer conventional blade, bar (rod) or roll type application methods. In addition, the present invention relates to a method of manufacturing multi-layer coated paper and paperboard for applications wherein functional coatings or additives, whether pigmented or non-pigmented, constitute one or more of the coating layers. Furthermore the present invention relates to the coated paper or paperboard obtainable by the processes of the present invention.

Prior Art:

[0002] The curtain coating method for the simultaneous coating of multiple layers is well known and is described in U.S. Pat. Nos. 3,508,947 and 3,632,374 for applying photographic compositions to paper and plastic web. But photographic solutions or emulsions have a low viscosity, a low solid content and are applied at low coating speeds.

[0003] In the manufacturing of printing paper usually pigmented coating compositions having a considerably higher solid content and viscosity compared to photographic solutions or emulsions are applied for example by blade type, bar type or reverse-roll type coating methods at high line speeds of above 1000 m/min. Any or all of these methods are commonly employed to sequentially apply pigmented coatings to the moving paper or paperboard surface.

[0004] However, each of these application methods inherently carries with them their own set of problems that can result in an inferior coated surface quality. In the case of the blade type coating method, the lodgment of particles under the blade can result in streaks in the coating layer, which lowers the quality of the coated paper or paperboard. In addition, the high pressure that must be applied to the blade to achieve the desired coating weight places a very large stress on the substrate and can result in the breakage of the substrate web, resulting in lowered production efficiency. Moreover, since the pigmented coatings are highly abrasive, the blade must be replaced regularly in order to maintain the evenness of the coated surface. Also, the distribution of the coating on the surface of the paper or paperboard substrate is affected by the surface irregularities of the substrate. An uneven distribution of coating across the paper or paperboard surface can result in a dappled or mottled surface appearance that can lead to an inferior printing result.

[0005] The bar (rod) type coating method has a limitation of solids content and viscosity of the pigmented coating color that is to be applied. Pigmented coatings applied by the bar type coating method are typically lower in solids content and viscosity than are pigmented coating colors applied by the blade type method. Accordingly, for the bar type coating method it is not possible to freely change the amount of coating that can be applied to the surface of the paper or paperboard substrate. Undesirable reductions in the quality of the surface of the coated paper or paperboard can result when the parameters of coating solids content, viscosity and coatweight are imbalanced. Moreover, abrasion of the bar by the pigmented coatings requires that the bar be replaced at regular intervals in order to maintain the evenness of the coated surface.

[0006] The roll type coating method is a particularly complex process of applying pigmented coatings to paper and paperboard in that there is a narrow range of operating conditions related to substrate surface characteristics, substrate porosity, coating solids content and coating viscosity that must be observed for each operating speed and each desired coatweight to be achieved. An imbalance between these variables can lead to an uneven film-split pattern on the surface of the coated paper, which can lead to an inferior printing result, or the expulsion of small droplets of coating as the sheet exits the coating nip. These droplets, if re-deposited on the sheet surface, can lead to an inferior printing result. Moreover, the maximum amount of coating that can be applied to a paper or paperboard surface in one pass using the roll type coating method is typically less than that which can be applied in one pass by the blade or bar type coating methods. This coating weight limitation is especially pronounced at high coating speeds.

Furthermore, all these methods have in common, that the amount of coating liquid applied to a paper web that generally has an irregular surface with hills and valleys is different whether applied to a hill or a valley. Therefore coating thickness and thus ink reception properties will vary across the surface of the coated paper resulting in irregularities in the printed image. Despite their drawbacks these coating methods are still the dominant processes in the paper industry due to their economics especially because very high line speeds can be achieved.

[0007] The Japanese patent applications JP-94-89437, JP-93-311931, JP-93-177816, JP-93-131718, JP-92-298683, JP-92-51933, JP-91-298229, JP-90-217327, and JP-8-310110 and EP-A 517 223 disclose the use of curtain coating methods to apply one or more pigmented coating layers to a moving paper surface. More specifically, the prior art relates to:

(i) The curtain coating method being used to apply a single layer of pigmented coating to a basepaper substrate to produce a single-layer-pigmented coating of paper.
(ii) The curtain coating method being used to apply a single priming layer of pigmented coating to a basepaper substrate prior to the application of a single layer of pigmented topcoat applied by a blade type coating process. Thus a multi-layer-pigmented coating of paper was achieved by sequential applications of pigmented coating.
(iii) The curtain coating method being used to apply a single topcoating layer of pigmented coating to a basepaper substrate that has previously been primed with a single layer of pigmented precoat that was applied by a blade or a metering roll type coating process. Thus a multi-layer-pigmented coating of paper was achieved by sequential applications of pigmented coating.
(iv) The curtain coating method being used to apply two single layers of specialised pigmented coating to a basepaper substrate such that the single layers were applied in consecutive processes. Thus a multi-layer-pigmented coating of paper was achieved by sequential applications of pigmented coating.

[0008] The use of a curtain coating method to apply a single layer of pigmented coating to the surface of a moving web of paper, as disclosed in the above discussed prior art, is stated to offer the opportunity to produce a superior quality coated paper surface compared to that coated by conventional means. However, the sequential application of single layers of pigmented coating using curtain coating techniques is constrained by the dynamics of the curtain coating process. Specifically, lightweight coating applications can only be made at coating speeds below those currently employed by conventional coating processes because at high coating speeds the curtain becomes unstable and an inferior coated surface results. Alternatively, the application of heavier coating weights can provide greater stability to the curtain and enable faster operating speeds. However, the total weight of coating that must be applied in order to achieve curtain stability at high speed is usually greater than that which is currently applied by conventional multi-layer coating processes. This is unacceptable from a coated paper quality perspective and from a coating economics perspective. Hence the conventional methods of producing multi-coated papers and paperboards employ the blade, rod or roll metering processes. However, application of consecutive single layers of pigmented coatings to paper or paperboard at successive coating stations, whether by any of the above coating methods, remains a capital-intensive process due to the number of coating stations required, the amount of ancillary hardware required, e.g., drive units, dryers, etc., and the space that is required to house the machinery.
[0009] Coated papers and paperboards that have received a coating that contains an additive designed to impart functional properties, such as barrier properties, optical properties e.g., color, brightness, opacity, gloss etc., release properties, adhesive properties and the like, are here described as functional products and their coatings may be referred to as functional coatings. The coating components that impart these properties may also be referred to as functional additives. Functional products include such types as self adhesive papers, stamp papers, wallpapers, silicone release papers, food packagings, grease-proof papers, moisture resistant papers, saturated tape backing papers, and the like.
[0010] In addition to photographic applications simultaneous application of multiple coatings by curtain coating methods is known from the art of making pressure sensitive copying paper. For example U.S. Patent No. 4,230,743 discloses in one embodiment simultaneous application of a base coating comprising microcapsules as main component and a second layer comprising a color developer as a main component onto a travelling web. But it is reported that the resulting paper has the same characteristics as the paper made by sequential application of the layers. Moreover, the coating composition containing the color developer is described as having a viscosity between 10 and 20 cps at 22°C.
[0011] JP-A-10-328613 discloses the simultaneous application of two coating layers onto a paper web by curtain coating to make an inkjet paper. The coating compositions applied according to the teaching of that reference are aqueous solutions with an extremely low solid content of about 8 percent by weight. Furthermore a thickener is added in order to obtain non-Newtonian behavior of the coating solutions. The examples in JP-A-10-328613 reveal that acceptable coating quality is only achieved at line speeds below 400m/min. The low operation speed of the coating process is not suitable for an economic production of printing paper especially commodity printing paper.
[0012] Although some improvements could be achieved by sequential coating steps using conventional coating techniques and/or curtain coating methods as discussed above, there is still a desire for further improvements with respect to printing quality of the resulting coated paper or paperboard and economics of the coating process.
[0013] Thus the object of the present invention is to provide a method for coating paper or paperboard, especially printing paper, resulting in improved quality of the coated product, that can be economically run at high line speeds

SUMMARY OF THE INVENTION

[0014] This object has been attained by a method of manufacturing multi-layer coated papers and paperboards, but excluding photographic papers and pressure sensitive copying papers, that are especially suitable for printing, packaging and labeling purposes, in which at least two coating liquids selected from aqueous emulsions or suspensions

are formed into a composite, free-falling curtain and a continuous web of basepaper or baseboard is coated with the composite coating liquid.

[0015] Preferably at least one the coating liquids comprises a binder.

[0016] The term "excluding photographic papers and pressure sensitive copying papers" should be interpreted in the sense that none of the coating liquids used in the practice of the present invention comprises silver compounds and that the coating liquids do not contain a combination of a microcapsuled color former and a color developer in a single coating liquid or in different coating liquids forming subsequent coating layers.

[0017] Furthermore the present invention refers to a paper or paperboard having at least two coating layers obtainable by a method according to present invention.

[0018] The coating liquids can be simultaneously applied according to the present invention by using a curtain coating unit with a slide nozzle arrangement for delivering multiple streams of coating liquid to form a continuous, multi-layer curtain. Alternatively an extrusion type supplying head having several adjacent extrusion nozzles can be employed in the practice of the present invention.

DESCRIPTION OF PREFERRED EMBODIMENTS

[0019] In the following the term paper also encompasses paperboard.

[0020] According to a preferred embodiment of the present invention at least one of the coating liquids forming the composite free falling curtain is pigmented. Preferably in making a paper for printing purposes at least two of the coating layers are pigmented. Additionally a top layer for improving surface properties like gloss or smoothness that is not pigmented might be present. But for the manufacturing of commodity printing paper coating with two pigmented layers is for the most purposes sufficient.

[0021] The present inventors have surprisingly discovered that the multi-layer coated paper or paperboard that has at least two layers of pigmented coating applied simultaneously to the surface has superior coated surface printing properties compared to multi-layer coated papers or paperboards manufactured by conventional coating methods such as blade, bar, roll or single-layer curtain coating methods as taught in the prior art discussed above.

[0022] The pigments useful in the process of the present are selected from clay, kaolin, talc, calcium carbonate, titanium dioxide, satin white, synthetic polymer pigment, zinc oxide, barium sulphate, gypsum, silica, alumina trihydrate, mica, diatomaceous earth. Kaolin, talc, calcium carbonate, titanium dioxide, satin white and synthetic polymer pigments are particularly preferred.

[0023] According to a particularly preferred embodiment the coating liquid forming the uppermost layer comprises a glossing formulation. This is especially useful in the present invention because the curtain coating generally results in a contour coating which provides high fibre coverage but low gloss. The novel combination of glossing formulation and simultaneous multilayer curtain coating combines the previously discussed advantages of curtain coating with good gloss.

[0024] The glossing formulations useful in the present invention comprise gloss additives, such as synthetic polymer pigments produced by polymerization of styrene, acrylonitrile and/or acrylic monomers. The synthetic polymer pigments have a glass transition temperature of 40 - 200° C, more preferably 50 - 130° C, and a particle size of 0.02 - 10 µm, more preferably 0.05 - 2 µm. The glossing formulations contain 20 - 100 weight-% gloss additive, more preferably 60 - 100 weight-%. Another type of glossing formulation comprises gloss varnishes, such as those based on epoxyacrylates, polyester, polyesteracrylates, polyurethanes, polyetheracrylates, oleoresins, nitrocellulose, polyamide, vinyl copolymers and various forms of polyacrylates.

[0025] Binders useful in the practice of the present invention are selected from styrene-butadiene latex, styrene-acrylate latex, styrene-butadiene-acrylonitrile latex, styrene-maleic anhydride latex, styrene-acrylate-maleic anhydride latex, polysaccharides, proteins, polyvinyl pyrrolidone, polyvinyl alcohol, polyvinyl acetate, cellulose and cellulose derivatives . Examples for polysaccharides are starch, carboxymethylated starch, agar and sodium alginate. Examples for proteins that can be suitably employed in the process of the present invention are albumin, soy protein, and casein.

[0026] In addition to the above material, if necessary, one or more additives such as a dispersant, a lubricant, a water retention agent, a crosslinking agent, a surfactant, an optical brightening agent, a pigment dye or colorant, or a soluble dye or colorant or the like may be used.

[0027] Contrary to art of photographic papers or pressure sensitive copying papers the method of the present invention can be practiced with coating liquids having a viscosity in a wide range and a high solid content even at high coating speeds.

[0028] Thus according to a preferred embodiment of the present invention the viscosity of the coating liquid forming the uppermost layer is above 20 cps at 25°C. A preferred viscosity range is from 100 cps to 2000 cps at 25°C, more preferred from 200 cps to 1000 cps at 25°C.

[0029] Likewise the viscosity of the coating liquid forming the layer contacting the basepaper or baseboard is preferably higher than 200 cps at 25°C. An especially preferred range for the viscosity of the coating liquid forming the

layer contacting the basepaper or baseboard is from 230 cps to 2000 cps at 25°C

[0030] The solids content of the coating liquids to be applied according to the present invention can range from 20 to 75 wt-% based on the total weight of the coating liquid. According to a preferred embodiment the solid content of at least one of the coating liquids forming the composite free falling curtain is higher than 60 wt-% based on the total weight of the coating liquid.

[0031] A particular advantage of the present invention is, that by the simultaneous application of at least two coating layers by curtain coating very thin layers or in other words very low coating weights of the respective layers can be obtained even at very high application speeds. Therefore the coating weight based on the dry coating of the uppermost layer can be from 0.1 to 30 g/m^2, more preferred 0.5 to 30 g/m^2. and the coating weight based on the dry coating of the layer contacting the basepaper or baseboard can be from 0.1 to 30 g/m^2, more preferred 0.5 to 30 g/m^2.

[0032] In a particularly preferred embodiment of the present invention the coating weight based on the dry coating of the uppermost layer is lower than the coating weight based on the dry coating of the layer contacting the basepaper or baseboard. Preferably the coating weight based on the dry coating of the uppermost layer is less than 75%, more preferred less than 50% of the coating weight based on the dry coating of the layer contacting the basepaper or baseboard. Thereby a greater coating raw material efficiencies in the paper and paperboard coating operations is achieved. Unlike conventional coating processes, the simultaneous multilayer coating method of the present invention allows the use of much larger quantities of raw materials under an extremely thin top layer of more expensive raw materials without compromising the quality of the finished coated product.

[0033] According to another embodiment of the present invention at least one of the coating layers imparts functionality selected from printability, barrier properties, optical properties e.g., color, brightness, opacity, gloss, etc., release properties, adhesive properties and the like. Thereby a method of manufacturing a multi-layer coated paper or paperboard, that has at least two layers of coating applied simultaneously to the surface whereby one or more of the simultaneously applied coating layers is a functional coating, e.g., a barrier layer, a colored layer, an opacifying layer, an adhesive layer or the like, or one or more of the layers contains an additive to impart such functionality. Functional coatings that are very tacky in character would not normally be coated by conventional consecutive coating processes because of the tendency of the coating material to adhere the substrate to guiding rolls or other coating equipment. The simultaneous multi-layer method, on the other hand, will allow such functional coatings to be placed underneath a topcoat that shields the functional coating from contact with the coating machinery.

[0034] The functional coating liquids used in the present invention are characterized in that they contain at least one component that imparts functionality as defined above and have a solids content of up to 75% by weight, preferably from 20% to 75% by weight based on the total weight of the coating liquid and a viscosity of up to 3,000 cps, preferably 50 to 2,000 cps at 25°C. Moreover, the coated papers or paperboards produced by this method are characterized in that the top layer of applied coating has a dry weight of between 0.1 g/m^2 and 30 g/m^2, more preferred 0.5 to 30 g/m^2 and the under layers of coating have dry weights between 0.1 g/m^2 and 30 g/m^2, more preferred 0.5 to 30 g/m^2.

[0035] Also in the coating liquids forming the functional coatings of the present invention, a polymer of ethylene acrylic acid, a polyethylene, a polyurethane, a polyester, other polyolefins and the like, an adhesive such as a styrene butadiene latex, a styrene acrylate latex, a starch, a protein, or the like, a sizing agent such as a starch, a styrene-acrylic co-polymer, a styrene-maleic anhydride, a polyvinyl alcohol, a polyvinyl acetate, a carboxymethyl cellulose or the like, a barrier such as silicone, a wax or the like are used. The functional coating may include, but is not limited to include, a pigment or additive as previously described for a pigmented coating.

[0036] A pronounced advantage of the present invention irrespective of which embodiment is used is that the process of the present invention can be run at very high coating speeds that hitherto in the production of printing paper could only be achieved using blade, bar or roll application methods. Usual line speeds in the process of the invention are above 400 m/min, preferably, in a range of 600 - 3200 m/min, especially, from 800 to 2500 m/min.

[0037] One critical requirement for successful curtain coating at high speeds is that the kinetic energy of the falling curtain impacting the moving web be sufficiently high enough to displace the boundary layer air and wet the web to avoid air entrainment defects. This can be accomplished by raising the height of the curtain and/or by increasing the density of the coating. Hence, high speed curtain coating of low-density coatings such as a functional or glossing coating containing synthetic polymer pigment for improved gloss is difficult due to the lower kinetic energy and due to the fact that increasing the height of the curtain is limited by the difficulty of maintaining a stable uniform curtain. Low density coatings can be applied at high coating speeds with a curtain coating through the use of simultaneous multilayer coating in which a high-density carrier layer is used in combination with the low-density layer to achieve sufficiently high kinetic energy to avoid air entrainment. In addition simultaneous multilayer curtain coating allows the use of coating layers specifically designed to promote wetting of the substrate or to promote leveling of high solids coatings to further increase the high-speed operational coating window for paper and paperboard.

[0038] A further advantage of the present invention is, that a method of manufacturing a multi-coated paper or paperboard is provided that does not require the same level of high capital investment, the same amount of ancillary hardware or the same amount of space as is currently required by conventional multi-layer coating methods such as

blade, bar, and roll processes.

BRIEF DESCRIPTION OF DRAWINGS

[0039]

Figure 1 is an explanatory cross-sectional view of a curtain coating unit 1 with a slide nozzle arrangement 2 for delivering multiple streams 3 of coating liquid to form a continuous, multi-layer curtain 4. When a dynamic equilibrium state is reached, the flow amount of the coating liquids flowing into the slide nozzle arrangement 2 is completely balanced with the flow amount flowing out of the slide nozzle arrangement. The free falling multi-layer curtain 4 comes into contact with web 5 which is running continuously and thus the web 5 is coated with multiple layers of the respective coating liquids. The running direction of the web 5 is changed immediately before the coating area by means of a roller 6 to minimize the effect of air flow accompanying the fast moving web 5.

[0040] The present invention will now be explained in more detail with reference to the examples.

EXAMPLES:

[0041] The following materials were used in the coatings liquids: All percentages and parts are based on weight unless otherwise indicated.

- $CaCO_3$ 60: dispersion of calcium carbonate with particle size of 60% < 2 µm in water (Hydrocarb 60 ME available from Pluess-Stauffer, Oftringen, Switzerland), 77% solids.
- $CaCO_3$ 90: dispersion of calcium carbonate with particle size of 90% < 2 µm in water (Hydrocarb 90 ME available from Pluess-Stauffer), 77% solids.
- Clay A: dispersion of No. 2 high brightness kaolin clay with particle size of 80% < 2 µm in water (SPS available from Imerys, St. Austell, England), 66.5% solids.
- Clay B: dispersion of No. 1 high brightness kaolin clay with particle size of 98% < 2 µm in water (Hydragloss 90 available from J.M Huber Corp., Have de Grace, Maryland, USA), 71% solids.
- Synthetic polymer pigment: dispersion of polystyrene with particle size 0.26 µm (DPP 711 available from The Dow Chemical Company, Midland, Michigan, USA), 52% solids in water.
- Latex A: carboxylated styrene-butadiene latex (DL 950 available from The Dow Chemical Company), 50% solids in water.
- Latex B: carboxylated styrene-butadiene latex (DL 980 available from The Dow Chemical Company), 50% solids in water, 150 cps viscosity.
- Latex C: styrene-acrylate latex (XZ 94329.04 available from The Dow Chemical Company), 48% solids in water.
- Latex D: carboxylated styrene-butadiene latex (DL 966 available from The Dow Chemical Company), 50% solids in water.
- PVOH co-binder (synthetic co-binder): solution of 15% of low molecular weight synthetic polyvinyl alcohol (Mowiol® 6/98 available from Clariant AG, Basel Switzerland)
- Surfactant: aqueous solution of sodium di-alkylsulphosuccinate (Aerosol® OT available from Cyanamid, Wayne, New Jersey, USA), 75% solids.
- Whitener: fluorescent whitening agent derived from diamino-stilbenedisultonic acid (Blankophor® P available from Bayer AG, Leverkusen, Germany)

[0042] The pH of the pigmented coatings formulations was adjusted to 8.5 by adding NaOH solution (10%). The solids contents of the formulations were adjusted by adding water.

[0043] The above ingredients were mixed in the amounts given in Tables 1 and 2 respectively to obtain undercoat compositions (Formulations 1 to 6) and topcoat compositions (Formulations 7 to 12), respectively.

Table 1: Undercoat Formulations

Formulation	1	2	3	4	5	6
	Parts	Based	on	dry	weight	
$CaCO_3$ 60	100	50	100			
$CaCO_3$ 90		35			100	70
Clay A		15				30
Latex A	10	10	10		10	10
Latex B				100		
PVOH	1.2	0.3	1.0	1.0	1.0	0.3
Surfactant	0.5	0.4	0.4	0.8	0.4	0.4
Whitener			1.5		1.5	
Solids Content (%)	72.7	68.7	71.1	49.2	69.7	61.7
Viscosity (cps)	360	390	230	350	360	260
PH	8.5	8.5	8.5	8.5	8.5	8.5

Table 2: Topcoat Formulations

Formulation	7	8	9	10	11	12
	Parts	Based	on	dry	weight	
$CaCO_3$ 60		50				
$CaCO_3$ 90	70	35	30	100		70
Clay A	30	15				30
Clay B			70			
Synthetic Polymer Pigment					100	
Latex A	10	10				10
Latex B						
Latex C			11			
Latex D				10	26	
PVOH	0.3	0.3	0.7	1.0	1.0	0.4
Surfactant	0.4	0.4	0.4	0.4	0.8	0.4
Whitener			1.5	1.5		
Solids Content (%)	67.3	68.7	69.1	67.9	51.2	66.6
Viscosity (cps)	670	390	500	620	210	990
pH	8.5	8.5	8.5	8.5	8.5	8.5

[0044] The viscosities of Formulations 1 to 12 were determined as follows:

Brookfield Viscosity

[0045] The Brookfield viscosity was measured using a Brookfield RVT viscometer (available from Brookfield Engineering Laboratories, Inc., Stoughton, Massachusetts, USA) at 23°C. For measuring, 600 ml of the dispersion are poured into a 1000 ml beaker and the viscosity is measured at a spindle speed of 100 rpm.

[0046] The undercoat and topcoat formulations were coated onto paper according to the procedures described in the following examples. The properties of the coated papers were evaluated according to the following test procedures:

Paper Gloss

[0047] Paper gloss is measured using a Zehntner ZLR-1050 instrument at an incident angle of 75°.

Ink Gloss

[0048] The test is carried out on a Pruefbau Test Printing unit with Lorrilleux Red Ink No. 8588. An amount of 0.8 g/m^2 (or 1.6 g/m^2 respectively) of ink is applied to coated paper test strips mounted on a long rubber-backed platen with a steel printing disk. The pressure of the ink application is 1,000 N and the speed is 1 m/s. The printed strips are dried for 12 hours at 20°C at 55 % minimum room humidity. The gloss is then measured on a Zehntner ZLR-1050 instrument at an incident angle of 75°.

Dry Pick Resistance (IGT)

[0049] The test measures the ability of the paper surface to accept the transfer of ink without picking. The test was carried out on a A2 type printability tester, commercially available from IGT Reprotest BV. Coated paper strips (4 mm x 22 mm) are printed with inked aluminum disks at a printing pressure of 36 N with the pendulum drive system and the high viscosity test oil (red) from Reprotest BV. After the printing is completed, the distance where the coating begins to show damages is marked under a stereomicroscope. The marked distance is then transferred into the IGT velocity curve and the velocities in cm/s are read from the corresponding drive curve. High velocities mean high resistance to dry pick.

Ink Piling

[0050] Ink piling is tested on a Pruefbau printability tester. Paper strips are printed with ink commercially available under the trade name Huber Wegschlagfarbe No. 520068. A starting amount of 500 mm^3 is applied to an ink distribution roll. A steel printing disk is inked to achieve an ink volume of 60 mm^3. A coated paper strip is mounted on a rubber-backed platen and printed with the inked steel disk at a speed of 1.5 m/s and a printing pressure of 800 N. After a 10-second delay time, the paper strip is re-printed using a vulcanised rubber printing disk also containing 60 mm^3 of ink and at a printing pressure of 800 N. This procedure is repeated until the surface of the coated paper strip has ruptured. The number of printing passes required to rupture the coated paper surface is a measure of the surface strength of the paper.

Ink Mottling

[0051] This test is done to assess the print irregularity. Paper strips are printed on the Pruefbau Test Printing unit with test ink commercially available under the trade designation Huber Wegschlagfarbe No. 520068. First a volume of 250 mm^3 ink is applied with a steel roll. Then three passes using a vulcanized rubber roll follow and in each of those three passes an additional volume of 30 mm^3 of ink is applied. For evaluation of the mottling the strip is digitally analyzed using the Mottling Viewer Software from Only Solutions GmbH. First the strip is scanned and the scan is converted to a gray scale. Then the deviation in gray scale intensity is measured at seven different resolutions with a width of 0.17 mm, 0.34 mm, 0.67 mm, 1.34 mm, 2.54 mm, 5.1 mm and 10.2 mm. From these measurements a mottle value (MV) is calculated. The result shows the print irregularity. A higher number in the result means a higher irregularity.

Paper Roughness

[0052] The roughness of the coated paper surface is measured with a Parker PrintSurf roughness tester. A sample sheet of coated paper is clamped between a cork-melinex platen and a measuring head at a clamping pressure of 1,000 kPa. Compressed air is supplied to the instrument at 400 kPa and the leakage of air between the measuring head and the coated paper surface is measured. A higher number in the result indicates a higher degree of roughness of the coated paper surface.

Cobb Value

[0053] This test measures the water absorptiveness of paper and is conducted in accordance to the test procedure defined by the Technical Association of the Pulp and Paper Industry (T - 441). A pre-conditioned and pre-weighed sample of paper measuring 12.5 cm x 12.5 cm is clamped between a rubber mat and a circular metal ring. The metal ring is designed such that it circumscribes an area of 100 cm^2 on the paper sample surface. A 100-millilitre volume of

de-ionised water is poured into the ring and the paper surface allowed to absorb the water for a desired period of time. At the end of the time period the excess water is poured off, the paper sample removed, blotted and re-weighed. The amount of absorbed water is calculated and expressed as grams of water per square meter of paper. A higher number indicates a higher propensity for water absorption.

Coatweight

[0054] The coatweight achieved in each paper coating experiment was calculated from the known volumetric flow rate of the pump delivering the coating to the curtain coating head, the speed at which the continuous web of paper was moving under the curtain coating head, the density of the coating liquid, and the width of the continuous web of paper being coated.

Coating Density

[0055] The density of the coating liquid was determined by weighing a 100-millilitre sample of the coating in a pyknometer.

Comparative Examples 1 and 2 and Example 1:

[0056] To compare simultaneous multi-layer curtain coating versus single-layer curtain coating, woodfree basepaper was coated in three experiments in which the same total coatweight was applied in each of three ways, viz., consecutive single-layer coatings, simultaneous multi-layer coating, and one single-layer coating application.

Comparative Example 1:

[0057] Undercoat Formulation 1 was applied to the topside of a moving, continuous web of woodfree basepaper to achieve a coatweight of 10 ± 0.2 g/m^2. The basepaper web was moving at 900 m/min. After drying, the undercoated paper was topcoated with topcoat Formulation 7 to achieve a topcoat weight of 10 ± 0.2 g/m^2, also at 900 m/min. The topcoat was dried in a similar manner as the undercoat.

Example 1:

[0058] The same undercoat and topcoat formulations used in Comparative Example 1 were then applied simultaneously to the topside of the woodfree basepaper such that each coating layer achieved a coatweight of 10 ± 0.2 g/m^2. Coating speed was 900 m/min and drying was achieved using similar conditions as in Comparative Example 1.

Comparative Example 2:

[0059] Topcoat Formulation 7 was applied in a single layer application to the topside of the woodfree basepaper to achieve a coatweight of 20 ± 0.2 g/m^2. Coating speed was 900 m/min and drying was achieved using similar drying conditions used in Comparative Example 1.

[0060] The coated papers were all calendered under the same conditions and then tested for printing properties. Results from this series of trials are given in Table 3.

Table 3:

Examples	Comp. 1	1	Comp. 2
Undercoat Formulation	1	1	-
Topcoat Formulation	7	7	7
Web speed (m/min)	900	900	900
Undercoat Coatweight (g/m^2)	9.9	10.2	-
Topcoat Coatweight (g/m^2)	10.0	10.0	19.9
Single layer Application	Yes	-	Yes
Multi-layer Application	-	Yes	-

Table 3: (continued)

Examples	Comp. 1	1	Comp. 2
Paper Gloss (%)	53	66	67
Ink Gloss - 0.8 g/m^2 ink (%)	73	89	85
Ink Gloss - 1.6 g/m^2 ink (%)	75	94	90
Roughness (µm)	4.4	1.7	2.0
IGT Dry Pick (cm/s)	91	95	80
Ink Piling (No. of Passes)	3	5	4
Ink Mottling (Mottle Value)	7.8	6.4	6.5

[0061] The results in Table 3 show that the simultaneous multi-layer coated paper was superior in paper gloss, ink gloss, roughness, dry pick resistance, ink piling and ink mottling compared to the paper that received consecutive single layer applications of undercoat and topcoat. Moreover, the simultaneous multi-layer coated paper was superior in ink gloss, roughness, and dry pick resistance compared to the paper that received a single-layer coating of 20 g/m^2 of the relatively more expensive topcoat. The same advantages would be expected for coating of paperboard.

Examples 2 and 3

[0062] To determine whether a lightweight-coated paper could be produced by simultaneous multi-layer coating, a wood-containing basepaper was coated in two trials such that the total coatweight applied was similar to that which could be applied in conventional single-layer blade or curtain coating processes. The effect of increasing the relatively less expensive undercoat coatweight and decreasing the relatively more expensive topcoat coatweight on coated paper properties was examined by varying the ratio of undercoat coatweight to topcoat weight but with the total coatweight remaining constant.

Example 2:

[0063] Undercoat Formulation 3 and topcoat Formulation 9 were applied simultaneously to a continuous web of wood-containing basepaper such that each coating layer achieved a dry coatweight of 6.5 ± 0.1 g/m^2. Coating speed was 800 m/min. The coated paper was dried using similar drying conditions to those used in Example 1.

Example 3:

[0064] Undercoat Formulation 3 and topcoat Formulation 9 were applied simultaneously to wood-containing basepaper such that the undercoat achieved a coatweight of 9.8 g/m^2 and the topcoat achieved a coatweight of 3.3 g/m^2. Coating speed was again 800 m/min and the coated paper was dried as in Example 2.
Coated papers from Example 2 and 3 were calendered under the same conditions and then tested for printing properties. Results from this series of trials are given in Table 4.

Table 4:

Examples	2	3
Undercoat Formulation	3	3
Topcoat Formulation	9	9
Web speed (m/min)	800	800
Undercoat Coatweight (g/m^2)	6.5	9.8
Topcoat Coatweight (g/m^2)	6.6	3.3
Single layer Application	-	-
Multi-layer Application	Yes	Yes
Paper Gloss (%)	32	26

Table 4: (continued)

Examples	2	3
Ink Gloss - 0.8 g/m^2 ink (%)	45	35
Ink Gloss - 1.6 g/m^2 ink (%)	56	49
Roughness (µm)	4.2	4.4
IGT Dry Pick (cm/s)	47	58
Ink Piling (No. of Passes)	2	3
Ink Mottling (Mottle Value)	6.6	6.8

[0065] The results in Table 4 compare favourably with paper quality produced by other processes and are considered eminently suitable for printing purposes. Moreover, Example 3 demonstrates that acceptable coated paper properties were achieved by applying only half of the relatively expensive topcoat formulation applied in Trial Point 1. The results further demonstrate that simultaneous multi-layer coating enables the ratio of undercoat to topcoat to be varied significantly without impacting on the speed at which the web is coated. Application of a 3.3 g/m^2 coatweight at 800 m/min, as demonstrated in Example 3, is not achievable by single-layer curtain coating. In addition to the above observations it was found that the simultaneous multi-layer process could be run at more than twice the coating speed of other curtain coating processes.

<u>Example 4 and 5</u>

[0066] This was a repeat of Examples 2 and 3 but using woodfree basepaper and with a higher total coatweight target such as is typically applied to double coated woodfree papers and to coated paperboards produced by conventional coating methods. The objective of this experiment was to determine whether simultaneous multi-layer coating of a woodfree basepaper, in which a very low coatweight of a relatively expensive topcoat is applied to a very high coatweight of relatively less expensive undercoat, could produce acceptable paper properties for printing purposes.

Example 4:

[0067] Undercoat Formulation 3 and topcoat Formulation 9 were applied simultaneously to woodfree basepaper such that the undercoat achieved a coatweight of 18.6 g/m^2 and the topcoat achieved a coatweight of 6.8 g/m^2. Coating speed was 400 m/min.

Example 5:

[0068] Undercoat Formulation 3 and topcoat Formulation 9 were applied simultaneously to woodfree basepaper such that the undercoat achieved a coatweight of 21.7 g/m^2 and the topcoat achieved a coatweight of 3.5 g/m^2. Coating speed was 400 m/min.

[0069] Coated papers from Examples 4 and 5 were dried and calendered under similar conditions and then tested for printing properties. Results from this series of trials are given in Table 5.

Table 5:

Examples	4	5
Undercoat Formulation	3	3
Topcoat Formulation	9	9
Web speed (m/min)	400	400
Undercoat Coatweight (g/m^2)	18.6	21.7
Topcoat Coatweight (g/m^2)	6.8	3.5
Single layer Application	-	-
Multi-layer Application	Yes	Yes
Paper Gloss (%)	78	75

Table 5: (continued)

Examples	4	5
Ink Gloss - 0.8 g/m^2 ink (%)	94	90
Ink Gloss - 1.6 g/m^2 ink (%)	95	93
Roughness (µm)	1.2	1.5
IGT Dry Pick (cm/s)	71	75
Ink Piling (No. of Passes)	9	7
Ink Mottling (Mottle Value)	6.1	6.2

[0070] The results in Table 5 compare favourably with paper quality produced by other processes and are considered eminently suitable for printing purposes thus confirming the findings of Examples 2 and 3 in that the simultaneous multi-layer coating method enables the application of very light, relatively expensive topcoats over very heavy, relatively less expensive undercoats. It is also considered possible that the undercoat could be divided between several sub-layers where additional slots on the coating head are available. Such an approach would allow increased flexibility for designing and applying coating liquids with very specific properties. The same advantages would be expected for coating of paperboard.

Examples 6 and 7 and Comparative Example 3:

[0071] To determine whether simultaneous multi-layer coating could be used for applying a non-pigmented, functional coating that would otherwise not be possible to apply by conventional coating methods, an experiment was conducted in which a tacky undercoat with water-barrier properties was applied simultaneously with a pigmented topcoat to a woodfree basepaper.

Example 6:

[0072] Undercoat Formulation 4 and topcoat Formulation 10 were applied simultaneously to woodfree basepaper such that the undercoat achieved a coatweight of 4.0 g/m^2 and the topcoat achieved a coatweight of 10.1 g/m^2. Coating speed was 800 m/min.

Example 7:

[0073] Undercoat Formulation 4 and topcoat Formulation 10 were applied simultaneously to woodfree basepaper such that the undercoat achieved a coatweight of 3.9 g/m^2 and the topcoat achieved a coatweight of 7.5 g/m^2. Coating speed was 800 m/min.

Comparative Example 3:

[0074] Topcoat Formulation 10 was applied as a single curtain coating to woodfree basepaper such that the topcoat achieved a coatweight of 10.1 g/m^2. Coating speed was 800 m/min.
Coated papers from Examples 6 and 7 and Comparative Example 3 were dried and calendered under similar conditions and then tested for printing properties. Results from this series of trials are given in Table 6.

Table 6:

Examples	6	7	Comp. 3
Undercoat Formulation	4	4	4
Topcoat Formulation	10	10	10
Web speed (m/min)	800	800	800
Undercoat Coatweight (g/m^2)	4.0	3.9	-
Topcoat Coatweight (g/m^2)	10.1	7.5	10.1
Single layer Application	-	-	Yes

Table 6: (continued)

Examples	6	7	Comp. 3
Multi-layer Application	Yes	Yes	-
Paper Gloss (%)	48	45	39
Ink Gloss - 0.8 g/m² ink (%)	76	72	59
Ink Gloss - 1.6 g/m² ink (%)	82	82	66
Roughness (μm)	2.7	2.7	3.4
IGT Dry Pick (cm/s)	>110	>110	98
Ink Piling (No. of Passes)	10	10	6
Cobb Value (g H_2O/m^2)	10.9	10.0	45.4

[0075] The results in Table 6 demonstrate the suitability of the simultaneous multi-layer coating method for applying non-pigmented functional coatings to paper, such as a barrier coating, that would otherwise be unable to be applied by conventional coating methods or by consecutive single-layer curtain coating methods. The results clearly show that the application of the tacky undercoat significantly improved the overall strength of the coated paper, as measured by IGT dry pick and ink piling, and significantly decreased the water absorptiveness of the coated paper, as measured by the Cobb test.

Examples 8 and 9

[0076] It is hypothesised that the reduction in paper and ink gloss observed as topcoat coatweight is reduced could be compensated for by the optimisation of the topcoat pigment composition. To test this hypothesis, an experiment was conducted in which an undercoat formulation was topcoated with a very light, high-glossing topcoat formulation. The coatweight of the topcoat was significantly lower than that which can be achieved by conventional blade and single-layer curtain coating methods at the coating speed used.

Example 8:

[0077] Undercoat Formulation 5 and topcoat Formulation 11 were applied simultaneously to wood-containing base-paper such that the undercoat achieved a coatweight of 10.0 g/m² and the topcoat achieved a coatweight of 1.4 g/m². Coating speed was 800 m/min.

Example 9:

[0078] Undercoat Formulation 5 and topcoat Formulation 11 were applied simultaneously to wood-containing base-paper such that the undercoat achieved a coatweight of 10.0 g/m² and the topcoat achieved a coatweight of 0.7 g/m². Coating speed was 800 m/min.

[0079] Coated papers from Example 8 and 9 were dried and calendered under similar conditions and then tested for printing properties. Results from this series of trials are given in Table 7.

Table 7:

Examples	8	9
Undercoat Formulation	5	5
Topcoat Formulation	11	11
Web speed (m/min)	800	800
Undercoat Coatweight (g/m²)	10.0	10.0
Topcoat Coatweight (g/m²)	1.4	0.7
Single layer Application	-	-
Multi-layer Application	Yes	Yes

Table 7: (continued)

Examples	8	9
Paper Gloss (%)	73	70
Ink Gloss - 0.8 g/m² ink (%)	83	86
Ink Gloss - 1.6 g/m² ink (%)	89	90
Roughness (µm)	45	39
IGT Dry Pick (cm/s)	71	75
Ink Piling (No. of Passes)	2	2
Ink Mottling (Mottle Value)	6.6	7.4

[0080] The results from this experiment show that the application of an ultra-low coatweight of a high-glossing topcoat by the simultaneous multi-layer coating method can minimise the previously observed reduction in paper properties such as paper gloss and ink gloss. Specifically, a topcoat coatweight of less than 1 g/m^2 can be applied to achieve the desired coated paper properties. Conventional coating methods and single-layer curtain coating are unable to apply such low coatweights at such high speeds. The same advantages would be expected for coating of paperboard.

Claims

1. A method of manufacturing multi-layer coated papers and paperboards, but excluding photographic papers and pressure sensitive copying papers, that are especially suitable for printing, packaging and labeling purposes, in which at least two coating liquids selected from aqueous emulsions or suspensions are formed into a composite, free-falling curtain and a continuous web of basepaper or baseboard is coated with the composite coating liquid.

2. The method of claim 1, wherein
at least one of the coating liquids forming the composite free falling curtain comprises a binder.

3. The method of any of the preceding claims, wherein
at least one of the coating liquids forming the composite free falling curtain is pigmented.

4. The method of any of the preceding claims, wherein
the viscosity of the coating liquid forming the uppermost layer is higher than 20 cps at 25°C.

5. The method of claim 4, wherein
the viscosity of the coating liquid forming the uppermost layer is higher than 200 cps at 25°C.

6. The method of any of the preceding claims, wherein
the viscosity of the coating liquid forming the layer contacting the basepaper or baseboard is higher than 200 cps at 25°C.

7. The method of any of the preceding claims, wherein
the solid content of at least one of the coating liquids forming the composite free falling curtain is higher than 60 wt-% based on the total weight of the coating liquid.

8. The method of any of the preceding claims, wherein
the coating weight based on the dry coating of the uppermost layer is 0.1 - 30 g/m^2 and the coating weight based on the dry coating of the layer contacting the basepaper or baseboard is 0.1 - 30 g/m^2.

9. The method of any of the preceding claims, wherein
the coating weight based on the dry coating of the uppermost layer is lower than the coating weight based on the dry coating of the layer contacting the basepaper or baseboard.

10. The method of claim 8, wherein
the coating weight based on the dry coating of the uppermost layer is less than 75%, preferably less than 50% of

the coating weight based on the dry coating of the layer contacting the basepaper or baseboard.

11. The method of any of the preceding claims, wherein the coating liquid forming the uppermost layer comprises a glossing formulation comprising at least one gloss additive selected from synthetic polymer pigments and gloss varnishes.

12. The method of any of claims 3 - 10, wherein the pigment is selected from clay, kaolin, talc, calcium carbonate, titanium dioxide, satin white, synthetic polymer pigment, zinc oxide, barium sulphate, gypsum, silica, alumina trihydrate, mica, diatomaceous earth.

13. The method of any of the preceding claims, wherein the binder is selected from styrene-butadiene latex, styrene-acrylate latex, styrene-butadiene-acrylonitrile latex, styrene-maleic anhydride latex, styrene-acrylate-maleic anhydride latex, polysaccharides, proteins, polyvinyl pyrrolidone, polyvinyl alcohol, polyvinyl acetate, cellulose and cellulose derivatives

14. The method of any of the preceding claims, wherein at least one of the coating layers impart functionality selected from printability properties, barrier properties, optical properties, release properties, adhesive properties and the like.

15. The method of claim 14, wherein the coating liquid forming the coating layer that imparts functionality comprises one or more components selected from a polymer of ethylene acrylic acid, a polyethylene, a polyurethane, a polyester, other polyolefins and the like, a styrene butadiene latex, a styrene acrylate latex, a starch, a protein and the like, a styrene-acrylic co-polymer, a styrene maleic anhydride, a polyvinyl alcohol, a polyvinyl acetate, a carboxymethyl cellulose and the like, a silicone, a wax and microcapsules .

16. Paper or paperboard having at least two coating layers obtainable by a method according to any of claims 1-15.

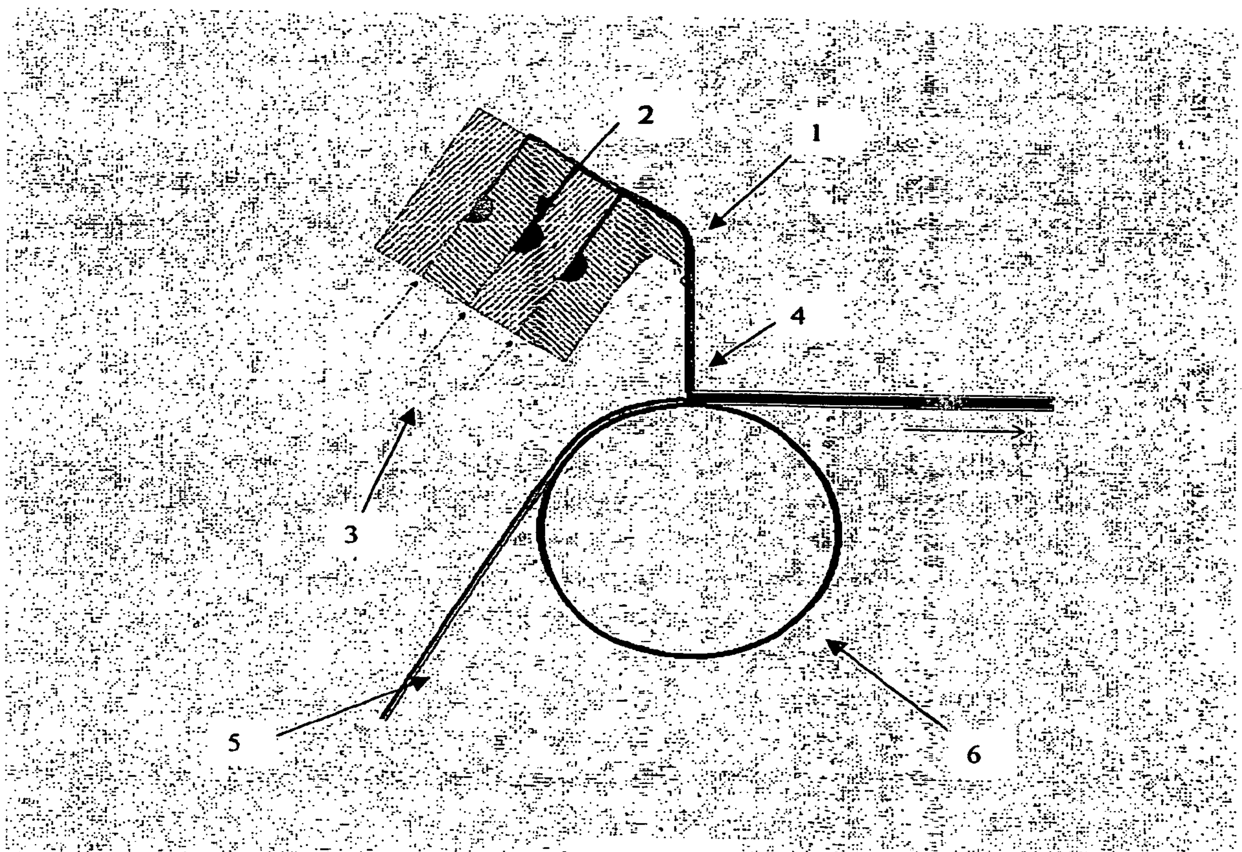

Fig. 1

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 01 10 9266

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
Y	GB 1 509 646 A (CIBA GEIGY AG) 4 May 1978 (1978-05-04) * the whole document *	1-10, 12-16	D21H23/48 D21H19/82
Y	EP 0 517 223 A (JUJO PAPER CO LTD) 9 December 1992 (1992-12-09) * the whole document *	1-10, 12-16	
A	US 4 109 611 A (FAHRNI FRITZ ET AL) 29 August 1978 (1978-08-29)		
A,D	US 3 508 947 A (HUGHES DONALD J) 28 April 1970 (1970-04-28)		
A,D	US 3 632 374 A (GREILLER JACK FRANCIS) 4 January 1972 (1972-01-04)		

TECHNICAL FIELDS SEARCHED (Int.Cl.7)
D21H

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	25 September 2001	Songy, O

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03 82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 01 10 9266

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

25-09-2001

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 1509646 A	04-05-1978	CH 591902 A5	14-10-1977
		FR 2310809 A1	10-12-1976
		US 4041897 A	16-08-1977
EP 0517223 A	09-12-1992	JP 2841923 B2	24-12-1998
		JP 4361696 A	15-12-1992
		CA 2070613 A1	08-12-1992
		DE 69213828 D1	24-10-1996
		DE 69213828 T2	30-01-1997
		DE 517223 T1	16-12-1993
		EP 0517223 A1	09-12-1992
		US 5447753 A	05-09-1995
US 4109611 A	29-08-1978	CH 613879 A5	31-10-1979
		BE 852965 A1	29-09-1977
		DE 2614068 A1	06-10-1977
		FR 2346057 A1	28-10-1977
		GB 1522914 A	31-08-1978
		JP 52117936 A	03-10-1977
US 3508947 A	28-04-1970	AR 197770 A1	10-05-1974
		AT 324119 B	11-08-1975
		BE 733012 A	13-11-1969
		CH 520532 A	31-03-1972
		DE 1928031 A1	11-12-1969
		DK 125070 B	27-12-1972
		FR 2010052 A5	13-02-1970
		GB 1276381 A	01-06-1972
		IL 32253 A	31-05-1973
		JP 49024133 B	20-06-1974
		NL 6908441 A	05-12-1969
		SE 363907 B	04-02-1974
		SU 399154 A3	27-09-1973
		SU 419008 A4	05-03-1974
		US 3867901 A	25-02-1975
US 3632374 A	04-01-1972	AT 317670 B	10-09-1974
		BE 733011 A	13-11-1969
		BE 733012 A	13-11-1969
		CH 520954 A	31-03-1972
		CH 520532 A	31-03-1972
		DE 1928025 A1	18-12-1969
		DK 125070 B	27-12-1972
		ES 367851 A1	16-02-1972
		ES 367852 A1	01-07-1971
		FR 2010051 A5	13-02-1970

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 01 10 9266

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

25-09-2001

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 3632374 A		FR 2010052 A5	13-02-1970
		GB 1276144 A	01-06-1972
		GB 1276381 A	01-06-1972
		IL 32253 A	31-05-1973
		IL 32272 A	30-07-1973
		JP 53031005 B	30-08-1978
		JP 49035447 B	21-09-1974
		JP 49024133 B	20-06-1974
		NL 6908441 A	05-12-1969
		NL 6908442 A	05-12-1969
		SE 364124 B	11-02-1974
		SE 363907 B	04-02-1974
		SU 399154 A3	27-09-1973
		SU 372778 A3	01-03-1973
		SU 419008 A4	05-03-1974
		US 3867901 A	25-02-1975

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82